

WHAT IS CLAIMED IS:

1 1. A mass spectrometry ionization method comprising:
2 delivering electrospray droplets from an electrospray nozzle, wherein the electrospray
3 droplets contain solvent and analytes; and
4 exposing the electrospray droplets to an ion beam thereby increasing the unbalanced
5 charge of the electrospray droplets.

1 2. A mass spectrometry ionization method comprising:
2 directing an ion beam at a solid sample matrix containing analyte thereby adding
3 unbalanced charge to the analyte and sample matrix; and
4 desorbing the charged analyte with a desorption laser.

1 3. A mass spectrometry ionization method comprising:
2 directing an ion beam at a liquid or solid sample matrix containing analyte thereby
3 ionizing and adding unbalanced charge to the analyte.

1 4. The method of claim 3 further comprising directing the charged analyte
2 through the interface of the mass spectrometer in synchrony with the duty cycle of the ion
3 detector.

1 5. The method of claim 3 or 4 wherein the analyte is deposited upon discrete
2 apices of the sample surface.

1 6. The method of claims 3 to 5 wherein the sample comprises bacteria, viruses or
2 cells.

1 7. The method of claims 1 to 6 wherein the ion beam consists of protons
2 whereby the analyte is protonated.

1 8. The method of claims 1 to 6 wherein the ion beam consists of anions or
2 electrons whereby the analyte is deprotonated.

1 9. The method of claim 1 wherein the sample is injected directly into the
2 focusing quadrupoles.

1 10. The method of claim 7 wherein the analyte comprises organic compounds
2 having nitrogen, oxygen, or sulfur heteroatoms.

1 **11.** The method of claims 1 to 10 wherein the ion beam flux is from about 1
2 mA/cm² to about 17 mA/cm².

1 **12.** The method of claims 1 to 11 wherein the ion beam energy is from about 5 to
2 about 50 electron volts.

1 **13.** The method of claim 12 wherein the ion beam energy from about 5 to about
2 10 electron volts.

1 **14.** The method of claim 1 wherein the electrospray flow rate is from about 0.025
2 µL/min to about 0.5 µL/min.

1 **15.** The method of claims 1 to 7 and 9 to 14 wherein the positive ions comprise
2 protons, lithium ions, or cesium ions.

1 **16.** The method of claim 8 where the anions comprise NH₂⁻ or H₃Si⁻.

1 **17.** The method of claim 2 wherein the sample matrix comprises a material of
2 Table 2.

1 **18.** A mass spectroscopy system comprising:
2 an analyte ion source;
3 an ion beam;
4 a mass analyzer; and
5 an ion detector.

1 **19.** A mass spectroscopy system comprising:
2 an analyte sample;
3 an ion beam;
4 a mass analyzer; and
5 an ion detector.